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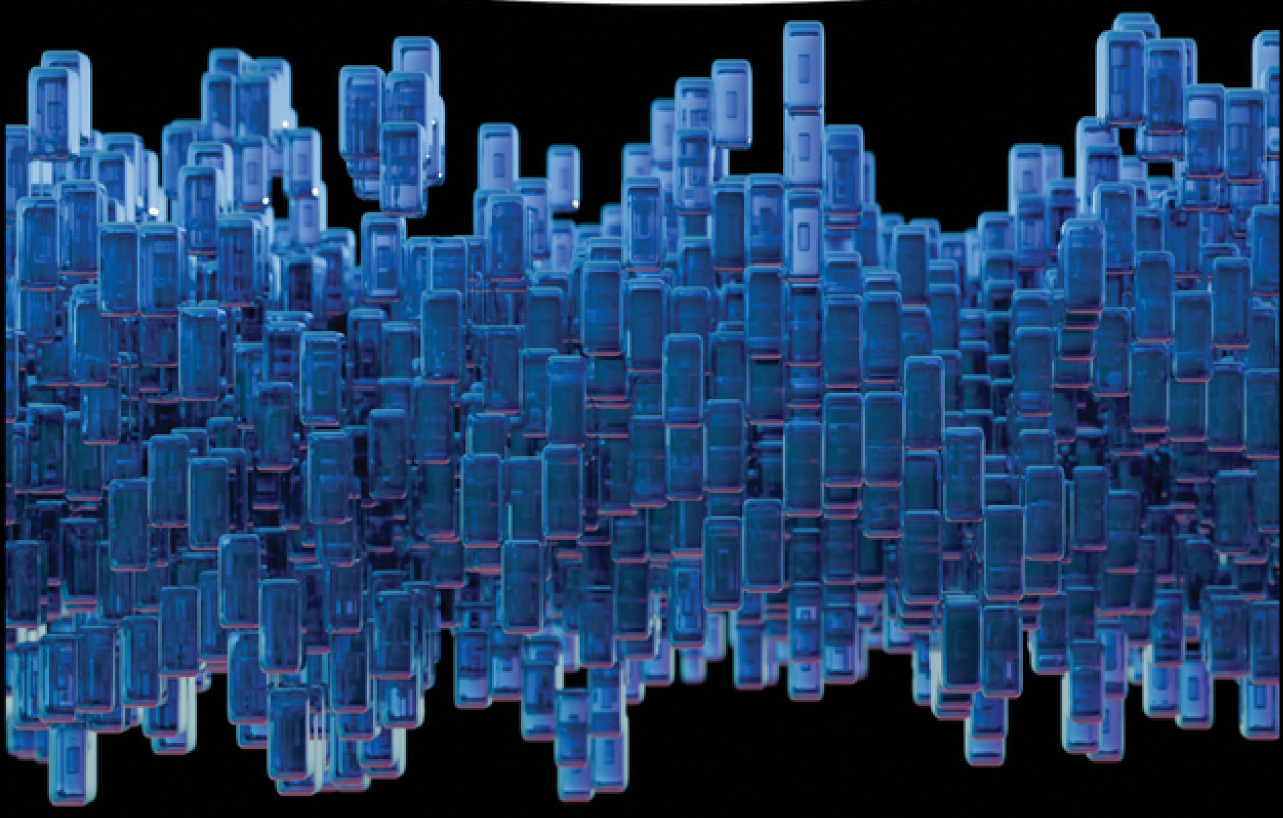
Bio-Nanomaterials in Environmental Remediation

Industrial Applications



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Brief Biography of Editors

Dr. Narendra K. Sharma

Dr. Narendra K. Sharma is working as assistant professor at the Department of Biosciences and Biotechnology of the Banasthali Vidyapith, India. He has done a PhD from Defence Institute of Physiology and Allied Sciences, DRDO, India, and post-doctoral training from Guangzhou Institutes of Biomedicine and Health (GIBH), CAS, China, and Federal University of Sao Paulo (UNIFESP), Brazil. He has more than eight years of teaching and research experience. He has published more than 50 research articles in peer-reviewed international journals, books, and book chapters. He has presented his research work at various international conferences held in India, Brazil, China, USA, and Germany.

He has been conferred several prestigious awards including Dr. T S Vasundhara memorial best paper award, DRDO, Young Scientist and Best Innovator award by Microbiologist Society of India, nominated as best innovator by Indian Academy of neuroscience, and travel award from Japan Neuroscience Society.

Dr. Rekha Sharma

Dr. Rekha Sharma received her B.Sc. from the University of Rajasthan, Jaipur, in 2007. In 2012, she completed her M.Sc. in Chemistry from Banasthali Vidyapith. She was awarded a Ph.D. in 2019 by the same university under the supervision of Prof. Dinesh Kumar. Presently, she is working as an assistant professor in the Department of Chemistry, Banasthali Vidyapith, and has entered a specialized research career focused on developing water purification technology. With more than six years of teaching and research experience, she has published 16 articles in journals of international repute, 1 authored book with CRC Press, and over 60 book chapters in the field of nanotechnology. She has presented her work at more than 15 national and international conferences. Dr. Sharma has reviewed many renowned Journals, Elsevier, Bentham Science, and Springer Nature, Science Direct, Trends in Carbohydrate Research. She has been recognized as a Young Women Scientist by the Department of Science and Technology (DST), Government of Rajasthan. Her research interest includes developing water purification technology by developing biomaterial-reduced NPs and polymers and biopolymers incorporated metal oxide-based nanoadsorbents and nanosensors to remove and sense health-hazardous inorganic toxicants like heavy metal ions from aqueous media for water and wastewater treatment.

She has presented her work in more than 15 national and international conferences. Her research interest includes the development of water purification technologies by the fabrication of nanosensors and nano-adsorbents for water and wastewater treatment, and the remediation of microplastics.

Dr. Tikam C. Dakal

Dr. Tikam C. Dakal is currently working as an assistant professor at Department of Biotechnology, Mohanlal Sukhadia University (Rajasthan), India. Dr. Dakal pursued his PhD from the University of Modena and Reggio Emilia, Italy, and did post-doctoral training from University of Montreal (Canada) and University of Bordeaux (France). Dr. Dakal has also served as a Staff Scientist at Beckman Research Institute of the City of Hope, California (USA). He has more than 10 years of teaching and research experience. Currently, Dr. Dakal is working in the field of Genome and Computational Biology with a focus on analyzing the biological/clinical data for deciphering the molecular basis of complex pathologies, for instance, cancers, neurodegenerative disorders, and others.

Dr. Dakal has been listed among top-2% scientists of the world by Stanford University for past 3 years. Dr. Dakal has published over 100 research/review articles in reputed journals. He has also edited 1 book and published some book chapters in books from reputed publishers. Dr. Dakal is recipient of prestigious HMR Foundation Fellowship at University of Montreal (Canada) and FEMS-Young Scientist Award by VAAM, Germany.

Preface

“There’s Plenty of Room at the Bottom”-Richard Feynman. One of the biggest challenges facing the modern world is environmental pollution and degradation caused by several sources. Numerous conventional techniques and tools are being used to address this issue. The field of nanotechnology has witnessed remarkable advancements, revolutionizing various sectors across science, technology, industry, and environmental conservation. At the heart of this transformation lies the incredible potential of bio-nanomaterials engineered at the atomic or molecular scale. The book entitled “Bio-Nanomaterials in Environmental Remediation: Industrial Applications” edited by Dr. Narendra K. Sharma, Dr. Rekha Sharma, and Dr. Tikam C. Dakal explores some of the exciting applications of bio-nanomaterials across different domains. The present book is focused majorly on the application of bio-nanomaterials in different industrial applications. This book contains a detailed coverage of the classification, properties, synthesis, cutting edge applications, and future perspectives of bio-nanomaterials to enhance readers’ understanding. To attract a wider readership and achieve the overall goal, the first chapter of the book provides a description of fundamentals and an up-to-date overview of the main subject of this book, i.e., introduction to bio-nanomaterials. This book also will cover use of bio-nanomaterials in various industrial fields for the reader-free quantification of poisonous substances in water, the remarkable application of different bio-nanomaterials in water remediation, textile industry, oil industry, gas industry, food industry, and agriculture industry as well as in determination of hazard, toxicity, and monitoring standards of the bio-nanomaterials. Despite our best efforts, mistakes and misconceptions may have occurred, for which we apologize. We welcome constructive criticism and suggestions to improve the presentation.

Dr. Narendra K. Sharma
Dr. Rekha Sharma
Dr. Tikam C. Dakal

1

Bio-nanomaterials: An Introduction

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1.1 Introduction

A bio-nanomaterial encompasses a diverse array of biological molecules and components, such as proteins, antibodies, enzymes, nucleic acids, lipids, polysaccharides, oligosaccharides, viruses, and secondary metabolites, organized at the molecular level to form materials with unique properties and functions [1, 2]. Nanotechnology, a multidisciplinary domain focused on materials at the nanometer scale (1–100 nm), has experienced significant advancements in recent years [3]. This field has diverse applications that extend across a wide spectrum of scientific fields, demonstrating its extensive impact and significance. The term "nanotechnology" stems from the Greek word "nano," denoting one-billionth of a meter, coined by Norio Taniguchi in 1974. This field has significantly advanced medicine by introducing nanosized particles and materials known for their exceptional biocompatibility and minimal toxicity, offering promising avenues for medical innovation and treatment. Bio-nanomaterials are the term assigned to nanosized materials, either composed of or produced through biological means. Nanoparticles, due to their minute size, exhibit extraordinary attributes across various domains including structure, chemistry, physics, optics, heat conductivity, mechanical strength, and electrical conductivity. Their distinctive characteristics position them as versatile tools in the biomedical sector, playing crucial roles in tasks such as advancing tissue engineering, regenerative medicine techniques, drug and gene delivery systems, cancer treatment modalities, and neurodegenerative disease therapies, thereby offering innovative solutions for addressing complex medical challenges [4]. For instance, drug delivery systems are designed to release drugs on target; gene therapy uses vectors that specifically enter targeted cells; cancer treatment employs nanoparticles (NPs) that selectively destroy tumor cells selectively; neurodegenerative diseases are addressed via therapeutic strategies that target specific pathological accumulations andinflammation is managed by therapeutic

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agents that regulate host immune responses among other possible causes of illnesses [5]. Furthermore, various bio-nanomaterials are utilized as diagnostic tools for identifying various biomarkers or as imaging agents for medical examinations.

Many biodegradable polymers and naturally sourced nanomaterials have been widely employed across biomedical, pharmaceutical, industrial, packaging, and agricultural sectors for the development of bio-nanomaterials. Manipulating materials at the nanoscale now enables fundamental interactions with biological systems, paving the way for customized medication delivery. This breakthrough opens avenues for precise and efficient illness treatment while minimizing adverse effects. Furthermore, bio-nanomaterials are essential in the creation of biosensors and imaging agents, which transform diagnostic methods and make it possible to identify various medical disorders early [6]. Hence, a wide array of biodegradable polymers and naturally derived nanomaterials have found extensive applications across diverse sectors, including biomedical, pharmaceuticals, industrial packaging, and agriculture (Figure 1.1). The utilization of bio-nanomaterials can be traced back to ancient Indian literature, particularly in Ayurveda, a traditional system of medicine practiced in the Indian subcontinent since the 7th century. Ayurvedic treatments often incorporate metal ash, known as Bhasma, to address various diseases [7]. Bhasma comprises metallic or mineral preparations that are treated

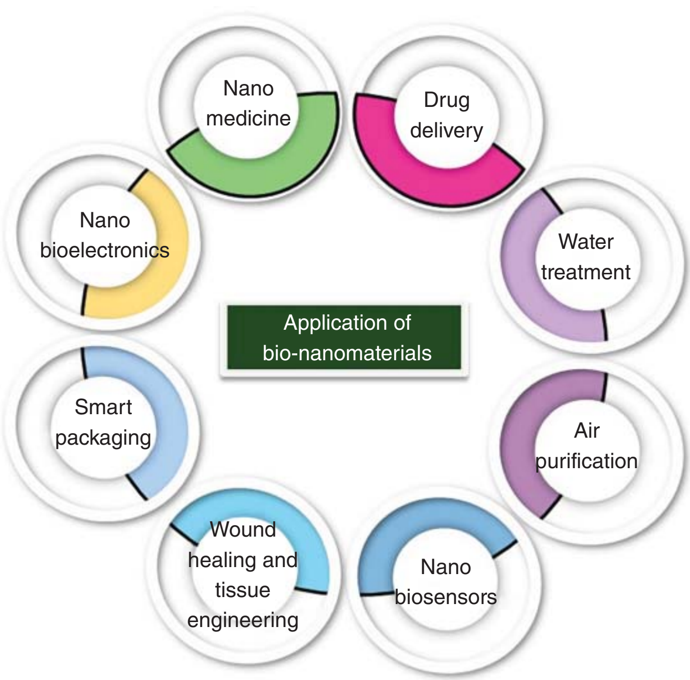

Figure 1.1 Applications of bio-nanomaterials. The figure illustrates the diverse range of applications of bio-nanomaterials across various fields, highlighting the versatility and potential impact of bio-nanomaterials, driving innovation and addressing pressing societal needs across diverse domains.

with herbal juices or decoctions and subjected to specific heating processes, as outlined in the puta system of Ayurveda. Widely recommended across India, Bhasma, a form of bio-nanomaterial, is administered either alone or in combination with medicinal plant extracts or powders, depending on the specific therapeutic needs of the patient [8]. Bio-nanomaterials exhibit diverse applications in environmental remediation, offering significant potential to address various environmental challenges. Both natural and artificial bio-nanomaterials possess unique attributes that can be harnessed to develop efficient and durable remediation methods. These materials hold promise in reducing pollution, restoring ecosystems, and promoting sustainable environmental practices.

The chapter involves the types of bio-nanomaterials, the various kinds of bio-nanomaterial conjugates, and the application of bio-nanomaterials in various fields ranging from health care and sustainable environmental technologies.

1.2 Types of Bio-nanomaterials

Bio-nanomaterials could be the derivatives of macro biomolecules (biological NPs) or they could be organic or inorganic compounds synthesized via the mediation of biological materials (derived bio-nanomaterials) (Table 1.1).

1.2.1 Classification of Biological Nanoparticles

Biological NPs are classified into four major categories derived from biomolecules or synthesized from organic building blocks, i.e. proteins, nucleic acids, lipids, and polysaccharides.

1.2.1.1 Proteins

Proteins are polymers of amino acids and can be the predecessor for the production of NPs, specifically oligopeptides composed of 8–20 amino acids. Due to their unique functionalities and the defined primary structure, these peptides are used for surface modification and attachment of various compounds that might be used for drugs and therapeutics [41, 42]. The ability of protein to form gels, emulsions, and dried particles, along with their capacity to synthesize NP with controlled size distribution, make them novel candidates for NP synthesis [43]. There are a number of proteins used for the NPs formulation: gelatin, elastin, collagen, gliadin, zein, ferritin, albumin, and silk protein (sericin and fibroin) [44–46].

By integrating principles from physics, engineering, chemistry, and biology, we have harnessed the capability to engineer biological nanomaterials at the molecular scale, utilizing self-assembling peptide systems. Peptides serve as the building blocks for creating a diverse array of nanostructures, including but not limited to nanofibers, nanotubes, vesicles, nanometer-thick surface coatings, and nanowires. Self-assembling peptides play multifaceted roles, ranging from stabilizing membrane proteins to creating favorable environments for cell growth and tissue repair in regenerative medicine. Moreover, they aid in gene and drug delivery, showcasing

Table 1.1 Overview of various strategies for biomolecule–nanoparticle integration.

S. no.	Material	Fabrication method	Particle size and characteristics	Application	References
1	Bovine serum albumin (BSA)	Dynamic aggregation, radiation-induced cross-linking	20–40 nm	Drug carrier	[9–11]
2	Cruciferin	Cold gelation	~200 nm spherical, polydispersity index (PDI) of 0.2–0.3	Delivery of bioactive food components	[12, 13]
3	Chimeric polypeptide	Genetically encoded synthesis in E. Coli	60 nm, nearly monodisperse	Treatment of cancer Conjugated drug: paclitaxel	[14–16]
4	Fibronectin	Electrospraying	28.2–31.52 nm	Functionally active protein for tissue engineering	[17–20]
5	Zein	Electrospraying	175–900 nm	Encapsulant for food coloring and ingredients	[21–25]
6	Fluorescent proteins	Liquid nanodispensing (NADIS)	50 nm–microns	Nanodevice (scanning probe lithography)	[26–28]
7	Fibroin	Electrospraying	80 nm	Wound dressing and tissue engineering	[29–31]
8	Whey protein isolate (WPI)	Homogenization-evaporation	90 nm	Delivery vehicle for beta-carotene to intestine	[26]
9	Chitosan oligosaccharide/β-lactoglobulin	Ionic gelation	150–30 nm, spherical	Delivery of hydrophobic bioactive compounds into aqueous foods	[32–35]
10	Bioactive peptides/chitosan	Ionic gelation	151 ± 4.3 nm, PDI = 0.05–0.14	Encapsulant of epigallocatechin-3-gallate (EGCG) for nanochemoprevention	[36, 37]
11	Chitosan	Ionic gelation	550–850 nm, spherical with some irregular shape particles	Protein carriers in tissue engineering	[38–40]

their versatility as tools for crafting sophisticated architectures, innovative materials, and nanodevices. These capabilities drive advancements in nanobiotechnology and various engineering disciplines. Positioned at the intersection of various disciplines such as chemistry, materials science, molecular biology, and engineering, molecular self-assembly harnesses nature's vast potential to advance across disciplines and enhance societal well-being. Nanofibers, elongated cylindrical structures measuring between 5 and 20 nm, possess a high surface-to-volume ratio that facilitates the incorporation of a wide array of bioactive molecules, including nucleic acids [47]. Among the peptides capable of self-assembly, examples include amyloid peptides, ionic self-complementary peptides, collagen-like triple helical peptides, and amphiphilic peptides, all of which can spontaneously organize into nanofibers [48].

1.2.1.2 Nucleic Acid

DNA and RNA possess the remarkable capability to form controlled and three-dimensional-oriented NPs. Their inherent affinity for complementary sequences allows nucleic acids to self-assemble into intricate, multidimensional structures with particular control over size and shape. This self-assembling ability results in the formation of compact and stable NPs, offering a versatile platform for various applications in nanotechnology and biomedicine [49]. The versatility and inherent characteristics of nucleic acids enable the precise engineering of single-stranded DNA or RNA molecules, resulting in the formation of modular nucleic acid nanoparticles (NANPs). These NANPs offer the flexibility to be intricately tailored into elaborate three-dimensional structures composed entirely of nucleic acids. RNA and DNA molecules assemble into diverse higher-order structures through both canonical and noncanonical base pairings, serving as the foundation for creating a range of nanostructures such as rings, fibers, and polygons [50–52]. By carefully choosing nucleic acid components, NANPs can be fine-tuned to modify their physicochemical properties, biological activities, and versatility. In the realms of biotechnology and biomedicine, NANPs emerge as promising carriers for bioactive compounds, tools for molecular imaging and biosensing, scaffolds for biochemical reactions, and multifunctional NPs amalgamating diverse functionalities within a unified structure.

The expanding domain of nucleic acid nanotechnology has brought forth a multitude of synthesis protocols tailored for NANPs, along with established classification methodologies enabling their study both in controlled laboratory environments and within living organisms. Moreover, compelling proof-of-concept data has emerged, underscoring their potential across diverse therapeutic applications [53–55].

1.2.1.3 Lipids

The fragmentation of lipids can give rise to various nanostructures, including liposomes, nanoemulsions, solid lipid nanoparticles (SLNs), and nanostructured lipid carriers (NLCs). These diverse lipid-based nanocarriers offer versatile platforms for drug delivery, enabling precise control over drug release kinetics, bioavailability, and targeting efficiency. These structures can be used for encapsulation of drugs to increase the efficiency by targeted delivery and preventing degradation of NPs [56, 57].

Liposomes, developed with an outer bilayer of amphipathic molecules like phospholipids enclosing an aqueous compartment, emerged as pharmaceutical products in the early nineties, with examples Alveofact® and Ambisome®. They possess several advantageous attributes as drug carriers: biological inertness, complete biodegradability, lack of toxicity, antigenicity, or pyrogenicity due to the natural presence of phospholipids in cell membranes. Additionally, liposomes can be tailored in terms of size, composition, and surface charge for specific applications, and they can encapsulate a wide range of hydrophilic and lipophilic drugs, offering possibilities for drug targeting. In the past two decades, SLNs, also known as lipospheres or nanospheres, have emerged as alternative particulate drug carrier systems, particularly suitable for lipophilic and poorly water-soluble drugs. With particle diameters ranging from approximately 10–1000 nm, SLNs combine the advantages of other carrier systems, including high biocompatibility, bioavailability, controlled release, physical stability, and protection of labile drugs from degradation. They are compatible with various administration routes such as oral, intravenous, pulmonary, and transdermal routes, thereby mitigating associated challenges [58].

1.2.1.4 Polysaccharides

Polysaccharides are a kind of carbohydrate polymers linked via glycosidic bonds. The most commonly used polysaccharide for NP is chitosan. Chitosan is a cationic polyaminosaccharide. Due to the presence of high-density amino groups and mucoadhesive properties, the reaction kinetics for the formation of new chemical bonds or negative complexation is very high [59]. The chitosan NPs easily conjugate with proteins, plasmid DNA, antigens, and bioflavonoids [60–62].

Polysaccharides, hydrophilic polymers derived from natural sources, are extensively employed in water-based polymer systems and nanotechnology owing to their advantageous attributes in biological settings. These include biodegradability, biocompatibility, and minimal toxicity, making them highly desirable for various applications. The exceptional properties of polysaccharides render them excellent candidates as building blocks for NP fabrication, particularly in medical therapy. The use of polysaccharides offers a plethora of benefits, such as high loading efficiencies, rapid drug release rates, precise targeting capabilities, remarkable stability, and minimal toxicity in physiological environments. Moreover, polysaccharides are abundant, easy to process, and derived from sustainable feedstocks, further enhancing their appeal. Chemical functionalization of polysaccharides, mainly via free carboxyl and hydroxyl groups, allows the creation of tailored polysaccharide derivatives with specific properties, facilitating their use in various applications. Various methodologies have been devised to synthesize polysaccharide-based NPs with precise control over size, morphology, and structure. These approaches encompass mechanisms such as ionic cross-linking, covalent cross-linking, self-assembly of hydrophobically modified polysaccharides, polyelectrolyte complexation, and the formation of polysaccharide–drug conjugates. The choice of synthetic route is crucial to optimize NP properties for specific applications, considering factors such as physicochemical parameters of polysaccharides, polysaccharide composition, NP size, and surface morphology. It is vital to note the distinction between NPs and nanocrystals, with NPs being amorphous particles and nanocrystals being crystalline, to avoid misunderstandings in terminology. While polysaccharide nanocrystals will not be discussed in detail, some useful applications will be mentioned [63].

1.2.2 Derived Bio-nanomaterials

There are various nanosized biomaterials that can be categorized as derived bio-nanomaterials. This is further categorized as the artificially synthesized nanomaterial mediated by biological compounds and the biological component which is part of organisms.

1.2.2.1 Green Synthesized Nanoparticles

Metal NPs can be developed via various chemical, physical, and radiation techniques. These methods encompass chemical reduction, precipitation, electrochemical deposition, sol-gel processes, physical vapor deposition, laser ablation, and irradiation-induced synthesis, among others. Each approach offers distinct advantages and allows for precise control over the size, shape, and properties of the resulting NPs, catering to specific applications in fields ranging from catalysis to biomedicine. The drawback associated with these methods is the potential for toxicity due to the use of certain chemicals, high temperatures, or radiation during the synthesis process. Metal and metal oxide NPs can be synthesized through the involvement of biological elements such as plant extracts, bacterial extracts, fungal extracts, seaweed, polysaccharides, biodegradable polymers, botanical materials, and algae. The green synthesis of NPs is a single-step process, environmentally benign, simple, economically viable, and clean technology as it does not involve harsh chemicals and zero harmful by-products. The biosynthetic pathways utilized for NP fabrication present a unique advantage by enabling the simultaneous reduction and stabilization of metal NPs within a single-step synthesis process [64].

1.2.2.2 Nanosize-Derived Component

Viruses, with sizes ranging from a few nanometers to hundreds of nanometers, present an intriguing avenue for various biomedical applications. Their surfaces can be modified and targeted for therapies such as cancer treatment, immune therapy, drug delivery, and detection. To date, only one viral therapy, T-VEC (Imlygic), a modified herpes simplex virus (HSV), has received Food and Drug Administration (FDA) approval for the treatment of cancer, specifically for subsets of patients with melanoma [65]. Viral nanoparticles (VNPs) encompass a diverse range of viruses, including plant viruses, bacteriophages, and mammalian viruses. Genome-free versions of VNPs, known as virus-like particles (VLPs), find utility in gene therapies, cancer therapies, antimicrobial therapies, immunotherapies, vaccines, cardiovascular therapies, imaging, and theragnostics [66].

1.3 Integration of Nanoparticles and Biomolecules

The size of biomolecules is comparable to NPs. The size similarity gives the advantage for the physical interaction with the NPs, which might lead to many noncovalent interactions such as ionic interaction, hydrophobic interaction, and solvation effect. Biomolecules, due to their intrinsic properties of donating electron clouds or accommodating excess negative charge, covalent bond formation, and stabilizing the volatile compound, lead to the formation of biomolecule–NP hybrids, which have characteristics of both NPs and biomolecules [67]. The intrinsic features of biomolecules could be used for the building block of NP architecture (Table 1.2). The protein molecules have various binding sites that could facilitate the development of multifunctional NPs [99].

1.3.1 Different Processes of Synthesis of Nanoparticles and Biomolecules Integration

1.3.1.1 Conjugation via Noncovalent Interactions

Noncovalent conjugation strategies are physical interactions involving electrostatic, hydrophobic, and affinity forces [100]. The ionic interaction between biomolecules and NPs offers a robust and stable approach to engineering desired complexes. This process involves either imparting the desired charge to NPs for binding with targeted biomolecules or binding biomolecules with charged ligands or specific buffers to enable binding with oppositely charged NPs [101]. For instance, to incorporate siRNA effectively, lipid NPs can be modified with supercharged coiled-coil arginine-rich proteins. This modification enables the NPs to interact with negatively charged RNA molecules, facilitating the encapsulation and delivery of siRNA for targeted gene silencing applications [102]. Another example is a self-assembled nanocomplex formed by negatively charged fucoidan (a sulfated polysaccharide) and positively charged protamine [103]. The advantage of a noncovalent electrostatic complex is the synergistic combination of functional properties of both.

Hydrophobic interaction also helps in binding of peptides onto the surface of silica at various pH conditions. By tuning the surface property of NPs and binding environment, the biomolecules adsorption on NPs can be regulated [104]. Similarly, gliadin, a protein NP can interact with Resveratrol via hydrophobic interaction [105].

1.3.1.2 Conjugation via Covalent Interactions

The covalent interaction that occurs between biomolecules and NPs is called chemisorption. In chemisorption, biomolecules having a thiol group (cysteine residue) can form a link with the NPs [106]. In instances where thiol residues are absent, a thiol group can be chemically introduced onto biomolecules using Traut's reagent (2-aminothiolane). This reagent enables site-specific modification by reacting with primary amines, facilitating the attachment of thiol groups for subsequent conjugation or functionalization processes [106, 107]. Noble metal NPs, especially gold (Au), are highly reactive to the thiol group. Au can form a strong bond with sulfur (Au—S). This has been exploited in forming various conjugates of Au NPs of peptides, DNA, antibodies, and proteins [99, 100, 108].